XAFS EXAMINATION OF MERCURY CAPTURE ON THREE ACTIVATED CARBONS

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INTRODUCTION

Mercury is listed as one of the eleven so-called "air-toxics" elements in the Amendments to the 1990 Clean Air Act [1]. Furthermore, as a result of research stimulated by the passage of this legislation, mercury is now regarded as the single trace element of greatest concern to utilities generating electrical power from coal combustion, despite its extremely low average concentration in most U.S. coals, typically 0.05 - 0.2 ppm [2,3]. The reasons for this concern include the volatility of mercury and its compounds, the toxicity of its compounds, the ease with which mercury can enter the food chain, particularly by accumulation in fish [4], and the huge volumes of coal consumed by the power generation industry, which is now approaching one billion tons/year in the U.S. [5].

One promising approach to reducing the atmospheric emission of mercury from coal combustion is the development of sorbent materials that efficiently capture mercury from combustion flue gases at relatively low temperatures (below 150°C). Of the many types of materials considered for such applications, activated carbons have been shown to be among the best. In this work, X-ray absorption fine structure (XAFS) spectroscopy has been employed to examine the mechanism of mercury capture on three different activated carbon sorbents. The element-specific nature of the XAFS technique has also enabled complementary information to be obtained on the behavior of other important elements present either in the flue gases or in the original carbons.

EXPERIMENTAL

(i) Mercury Sorption Experiments

Three different activated carbons were prepared at the University of North Dakota Energy and Environmental Research Center (EERC): a lignite-derived activated carbon (LAC), an iodine-activated carbon (IAC), and a sulfur-activated carbon (SAC). Aliquots of each of these carbons were used in various experiments at EERC to absorb mercury from a simulated combustion flue gas in a bench-scale reactor. In a typical experiment, about 400 mg of sorbent was held in the simulated flue gas at a temperature between 225 F and 325 F for a period of up to 16 hours. The baseline flue gas consisted of a synthetic mixture of 6% O_2, 12% CO_2, 1600 ppm SO_2, 50 ppm HCl, 8% H_2O, and the balance N_2. Elemental mercury was added to the baseline flue gas at a concentration of 60 $\mu g/m^3$, although some experiments were run with addition of $HgCl_2$ at 12 $\mu g/m^3$. Three different sets of experiments were performed: the first set consisted of a comparison of the three sorbents before and after exposure to the simulated flue gas; the second set consisted of the three sorbents exposed to a simulated flue gas containing mercuric chloride ($HgCl_2$); and the third set consisted of the LAC sorbent exposed to different formulations of the flue gas under otherwise identical conditions. Details of specific experiments are summarized in Table 1.

(ii) XAFS Experiments

The form of mercury and other elements present in the activated carbons before and after the sorption experiments were investigated using XAFS spectroscopy performed at either the Stanford Synchrotron Radiation Laboratory (SSRL), Palo Alto, CA, or the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, NY. At both synchrotrons, a 13-element germanium detector [6,7], gated electronically to record the L-edge fluorescence from mercury, was used to record the mercury L_{III} XAFS spectra. A 6μ gallium filter was also employed to maximize the signal/noise ratio. The XAFS spectra of other elements (S, Cl, Ca, I) were recorded at NSLS using a conventional Lytle fluorescence detector [8]. Zero-points of energy for the XAFS spectra of the different elements are defined as follows: sulfur K-edge - white line peak in elemental sulfur at 2,472 eV; chlorine K-edge - major derivative peak in NaCl at 2,825 eV; calcium K-edge - major derivative peak in $CaCO_3$ at 4,038 eV; iodine L_{III} edge - major derivative peak in elemental iodine (I_2) at 4,557 eV; and mercury L_{III} edge - major derivative peak in elemental mercury at 12,284 eV. Data reduction followed well established procedures [9,10]: first, the XAFS spectrum was divided into X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectral regions and each of these regions

was then examined separately. Whereas the XANES spectrum was used without further modification to identify elemental occurrences, the EXAFS spectrum was used to develop a "radial structure function" (RSF). The step-height, determined from the XAFS spectrum as the difference in background absorption above and below the edge, was used as a semi-quantitative measure of the relative concentration of the elements in different sets of samples (Table 2).

TABLE 1

Experimental Details for Sorption Experiments

Sample	Filter Temp. deg. F	Hg Species	Sorbent Mass mg	Flue Gas Hg Conc. $\mu g/m^3$	Gas Flow Rate m^3/hr	Length Test hr	Comments
IAC-1	225	Hg	300	60	0.85	3.37	
IAC-2	---	--	---	--	--	--	Unreacted
LAC-1	275	Hg	400	60	0.85	NA	
LAC-2	325	Hg	500	60	0.85	NA	
LAC-3	---	--	---	--	--	--	Unreacted
SAC-1	225	Hg	300	60	0.85	12.42	
SAC-2	---	--	---	--	--	--	Unreacted
IAC -400	225	$HgCl_2$	400	12	0.85	12.17	
LAC -400	225	$HgCl_2$	400	12	0.85	16.15	
SAC -400	225	$HgCl_2$	400	12	0.85	7.2	
LAC-5	225	Hg	400	60	0.85	4.0	10%O_2, bal. N_2
LAC-6	225	Hg	400	60	0.85	4.0	8%H_2O, 10%O_2, N_2
LAC-7	225	Hg	400	60	0.85	4.0	Baseline minus SO_2
LAC-8	225	Hg	400	60	0.85	4.0	Baseline minus HCl

TABLE 2

Relative Step-Heights Determined from XAFS Spectra

Sample	S	Cl	Ca	I	Hg
IAC-I	20			0.1	1
IAC-2	1			1	0
LAC-1	15	60	6.5	0	2.1
LAC-2	18	42	6.0	0	1.5
LAC-3	7	1		0	0
SAC-1	60		0.9	0	2.8
SAC-2	65		1	0	0
IAC (-400)					1.5
LAC (-400)					1.7
SAC (-400)					1
LAC-5					1.6
LAC-6					1
LAC-7					2.0
LAC-8					6.7

" " (blank) field indicates no determination made.
"0" indicates no significant edge detected for that element.

RESULTS AND DISCUSSION

(a) Sulfur

Sulfur XAFS experiments were carried out on the first suite of seven activated carbons (Table 2). Except for sample IAC-2, the sulfur XAFS spectra were quite strong and different forms of sulfur were readily apparent in the XANES spectra of different samples (Figure 1). Whereas the two SAC samples contained predominantly elemental sulfur (indicated by the major peak at 0 eV), the other samples (IAC-1, LAC) were predominantly sulfate sulfur (indicated by the major peak at 10 eV). The LAC samples also contained a minor amount (<10%) of elemental sulfur. The increase in step-height noted between IAC-1 and IAC-2 and between LAC-1, LAC-2 and LAC-3 suggests that the IAC and LAC carbons may absorb or react with SO_2, forming a sulfate species, during exposure to the flue gas. For the two SAC samples, however, there is little

change in sulfur concentration and, moreover, the sulfur form is elemental, which is not consistent with the sulfur speciation in the flue gas as SO_2.

(b) Chlorine
Chlorine XAFS experiments have been performed only on the three LAC samples in set 1. For the two samples (LAC-1, LAC-2) exposed to the flue gas, a significant increase (approx. 50 times) in chlorine concentration was indicated by the step-height data (Table 2). These data indicate that the LAC carbon readily absorbs chlorine. The chlorine XANES spectra are shown in Figure 2 and are consistent with the capture of chlorine as HCl and not as Cl_2 [11].

(c) Iodine
Iodine XAFS experiments were performed on all seven samples in set 1, but as expected, only the two IAC samples gave positive indications of iodine. The iodine L_{III} spectra are shown in Figure 3 and appear closest to elemental iodine, although the match is not exact. Whether this reflects a highly dispersed state for elemental iodine in the activated carbons remains to be demonstrated. The step-height data (Table 2) suggest that the iodine content of the carbon after exposure to the flue gas is much less than that before, which may indicate that significant volatilization of iodine from the carbon has occurred during exposure to the flue gas.

(d) Calcium
Calcium XAFS experiments were performed only on the two SAC samples and on the two LAC samples exposed to the flue gas. The step-height data for calcium (Table 2) indicate little or no difference in concentration for calcium between the two samples in each pair, suggesting that there is no net loss or gain of calcium during the exposure to the flue gas. The spectra (Figure 4) are distinct for each pair of samples. For the LAC samples, the calcium XANES spectra are similar to that from calcium sulfate ($CaSO_4$) [12]; however, the Ca form that gives rise to the spectra for the SAC samples is not so readily identified.

(e) Mercury
The mercury XANES spectra for the four carbon samples in the first sample set that were exposed to the simulated flue gas are shown in Figure 5. As with all mercury XANES spectra, the fine structure is rather subtle and the first derivative spectrum has been used to accentuate differences among the spectra. As can be seen from the figure, the fine structure becomes more prominent in the order IAC-1 < LAC-1, LAC-2 < SAC-1 and is accompanied by an increasing separation of the two peaks in the first differential spectra. Based on work on other mercury standards [13], it would appear that the separation of the peaks is highest for ionic mercury compounds and least for covalent and metallic mercury compounds. The observed trend for the peak separation in the activated carbons would be consistent with Hg-S or Hg-Cl bonding in the LAC-1, LAC-2 and SAC-1 carbons and Hg-I bonding in the IAC-1 carbon. Further evidence for this trend can be seen from an analysis of the EXAFS regions of the XAFS spectra presented in Figure 6. The radial structure functions (RSFs) shown in Figure 6 indicate a significantly different local structure for Hg in the iodine-impregnated carbon. In particular, the Hg-X bond for IAC-1 is much longer than those indicated for Hg in SAC-1 and for LAC-1,2. The peak positions in the RSFs are consistent with Hg^{2+}-Cl, as in $HgCl_2$, and/or Hg^{2+}-S, as in HgS (cinnabar), for the LAC-1,2 and SAC-1 samples, and with Hg^{2+}-I, as in HgI_2, for the IAC-1 sample. The Hg-S bond distance in HgS (cinnabar) is about 2.36 Å, the Hg-Cl bond distance in $HgCl_2$ is about 2.25 Å, and the bond distance for Hg-I in HgI_2 is about 2.78 Å.

Very similar mercury XANES spectra to those shown in Figure 5 were obtained from the second set of three samples (IAC -400, SAC -400, LAC -400) that were exposed to the flue gas containing $HgCl_2$. The close similarity of these spectra to those obtained from the corresponding samples exposed to the flue gas containing Hg vapor implies either that the mercury species in the flue gas is the same regardless of whether mercury or mercuric chloride is added to the flue gas, or that the products of the chemisorption reaction on the carbons are not determined by the speciation of mercury in the gas phase, but, rather, are determined by the active species on the carbons. It is also interesting to note that the step-heights derived from the XAFS spectra appear to correlate reasonably well with the durations of the experiments.

Except for differences in the mercury step-height (Table 2) or, equivalently, in the concentration of the mercury captured on the carbons, the spectral data for the LAC samples exposed to different formulations of the flue gas were closely similar to those of other LAC samples investigated previously. Since the experimental conditions were identical, except for the composition of the flue gas, the differences in the mercury step-height must reflect the relative efficiency with which mercury is captured from the gas stream. It would appear that moisture retards the absorption of mercury, but that HCl and especially SO_2 enhance the adsorption of elemental mercury. Further experiments will be carried out to confirm these observations.

CONCLUSIONS

This work demonstrates that XAFS spectroscopy is a powerful technique for identifying elemental species on activated carbons and for examining reactions involved in the adsorption of mercury from flue gases on such carbons. Although more work is needed to complete this investigation, a number of interesting conclusions appear to have been reached: (1) the mechanism involved in adsorption of mercury appears to depend on the element or method used to activate the carbon; (2) the LAC carbons are very efficient in extracting HCl from the flue gas and both the IAC and LAC carbons appear to react with SO_2 to form sulfate species; and (3) the adsorption of these gases by the carbons may also aid the adsorption of mercury as the rate of adsorption of mercury appears to be significantly affected by the composition of the flue gas.

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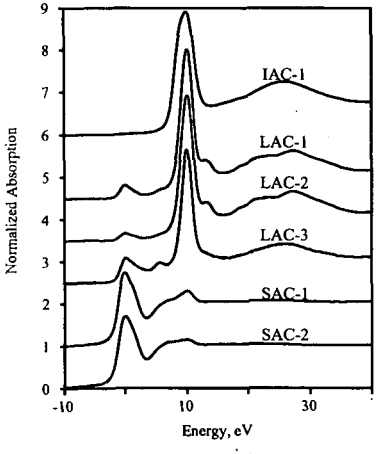

Figure 1: Sulfur XANES of activated carbons.

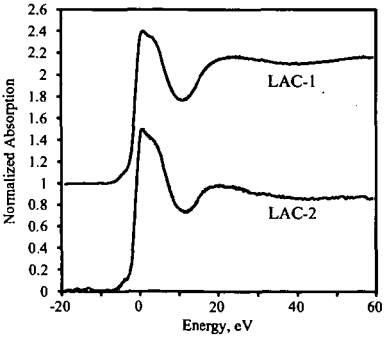

Figure 2: Chlorine XANES of LAC activated carbons.

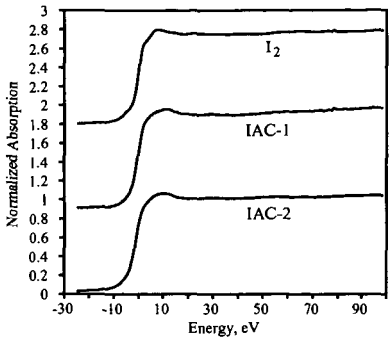

Figure 3: Iodine XANES of iodine activated carbons and elemental iodine (I_2).

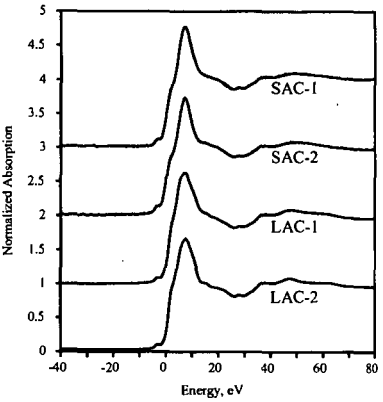

Figure 4: Calcium XANES of SAC and LAC carbons.

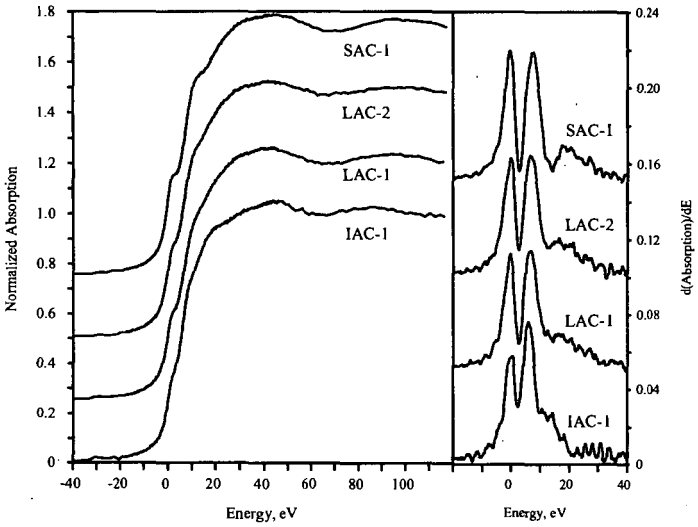

Figure 5: Mercury XANES and first derivative spectra of activated carbons exposed to simulated flue gas with mercury vapor.

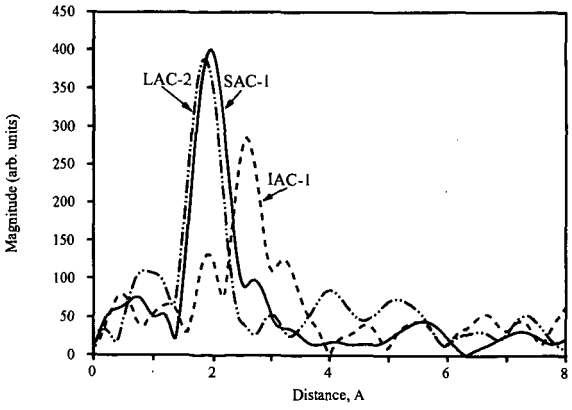

Figure 6: Radial structure functions for mercury in three activated carbons.